

Study of Zirconia Microporous Structure

V. Yu. Gavrilov

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received December 23, 1998

Abstract—The microporous structure of zirconium dioxide obtained by precipitation at different pH and different times of gel aging is studied by the physical adsorption of nitrogen, oxygen, and molecular hydrogen. It is shown that the ratio between the supermicropore surface areas measured by the adsorption of O₂ and N₂ as a function of the supermicropore volume previously revealed for SnO₂ is also retained for zirconia (the surface area of supermicropores measured by O₂ adsorption is larger than that measured by N₂ adsorption). Possible reasons for this phenomenon are discussed. The conclusions on the factors responsible for the formation of the zirconia microporous structure are drawn.

INTRODUCTION

Zirconia is widely used as a selective adsorbent, a support a number of catalysts for high-temperature processes and selective conversions, and an ion-exchanger with controlled adsorption properties [1–5]. Amorphous metals supported on ZrO₂ exhibit high activity in the low-temperature oxidation of CO [6].

The formation and retention of microporous structure is rather typical for zirconia obtained by precipitation, which is most often used now, especially for its low-temperature synthesis. Evidently, this affects the behavior of materials obtained in the majority of the processes. Therefore, studies of the properties of such xerogels by traditional adsorption methods with the use of conventional adsorbates and by other physical and chemical methods are of particular interest [7, 8].

The use of new experimental procedures for adsorption analysis, including the use of nontraditional adsorbates, leads to rather unexpected results. The results of our studies of tin dioxide xerogels [9] provide an example.

The goal of the present paper is to study the microporous structure of zirconia obtained by precipitation by comparison of data on the low-temperature (77.4 K) physical adsorption of N₂, O₂, and H₂.

EXPERIMENTAL

Zirconia samples were obtained by the traditional precipitation from an aqueous solution of zirconyl chloride, the most extensively employed zirconium compound, with a 12.5% aqueous solution of ammonia, along with vigorous stirring at constant temperature and pH (the concentration of the zirconyl chloride solution corresponded to 110 g (ZrO₂)/l). Prior to precipitation, the solutions of zirconyl chloride were heated. The gels obtained were washed with distilled water until chloride ions Cl⁻ were absent from the wash

water, extruded as granules, and dried in air and then in a drying oven at 150°C for 12–14 h.

The samples of ZrO₂ synthesized at 80°C in the pH range from 4 to 7 were chosen for the study. Our previous investigations [10] showed that, in this range of pH, xerogels with the largest volume of micropores were formed, whereas the volumes of meso- and macropores were quite small. In addition, the microtexture of several xerogels obtained at pH 4 and aged for a certain time (up to 22 h) in intermicellar medium was examined.

The adsorption isotherms of N₂, O₂, and H₂ at 77.4 K were measured with an automatic Digisorb-2600 Micrometrics instrument of the volumetric type. The samples were trained in a vacuum at 180°C for 6 h. To exclude a possible irreproducibility of textural parameters, the isotherms for different adsorbates were measured using the same weighed portions of samples for each set of samples.

The adsorption isotherms of nitrogen and oxygen vapors were treated by the traditional comparison method using the isotherms given in [11, 12] as reference isotherms. The adsorption isotherms of hydrogen were treated by the so-called comparative volumetric method proposed earlier in [13, 14].

RESULTS AND DISCUSSION

Figure 1 presents experimental adsorption isotherms of hydrogen on ZrO₂ samples precipitated in the cited pH range. These isotherms are completely reversible and thus point to the fact that the porous space of xerogels presents no diffusion problems for adsorbate molecules. The parameters of the microporous texture of zirconia xerogels (ultramicropore volume V_{up} and micropore volume V_{μ}) were calculated by the comparative volumetric method [14] taking into account the adsorption of H₂ on the surface of supermicro-, meso-,

Table 1. Parameters of the microporous structure of ZrO_2 samples precipitated at different pH (calculated from the hydrogen adsorption isotherms at 77.4 K)

Precipitation pH	V_μ , cm ³ /g
4	0.039
5	0.037
6	0.011
7	0

and macropores and using the equation

$$A - S_\alpha \alpha_{H_2} = V_{\mu\mu} + V_\mu \beta,$$

where A is the total adsorption of hydrogen, S_α is the surface area of pores traditionally measured by nitrogen adsorption, α_{H_2} is the specific adsorption of H_2 per unit surface, and β is the adsorption of hydrogen per unit micropore volume expressed in cm³ of H_2 at normal temperature and pressure (ntp) per cm³ of pore volume. The results of the calculation are presented in Table 1.

The volume of ultramicropores $V_{\mu\mu}$ was virtually zero. It was evaluated from the intercept on the ordinate on the plot of A versus $S_\alpha \alpha_{H_2} = f(\beta)$, which also involved the specific adsorption of H_2 . It will be shown below that the volume of micropores V_μ accessible to hydrogen molecules and determined from the slope of the same plot for the samples synthesized at pH 4 was somewhat larger than that accessible to nitrogen and

oxygen molecules. It may be assumed that this phenomenon is first of all due to molecular-sieve properties of zirconia xerogels. In fact, the kinetic diameter of hydrogen molecules is markedly smaller than those of nitrogen and oxygen molecules ($\sigma_k = 0.289, 0.364,$ and 0.346 nm, respectively [15]).

The trend to a decrease in V_μ with an increase in precipitation pH was also retained; thus, at pH higher than 6, micropores measured by hydrogen adsorption completely disappeared and the observed consumption of hydrogen was caused only by adsorption on the surface of supermicro- and mesopores S_α .

Oxygen and nitrogen were adsorbed at 77.4 K on zirconia xerogels obtained at pH 4 and aged for different times at the gel stage and also on the set of samples precipitated at a constant pH in the range from 4 to 7 without subsequent aging.

Figures 2 and 3 present typical adsorption isotherms for oxygen and nitrogen on freshly precipitated samples and on the samples subjected to aging. It is seen that a significant discrepancy (irreversibility over a wide range of pressures) between the adsorption and desorption branches, especially pronounced in nitrogen adsorption; for O_2 , it was observed only for freshly precipitated samples. As the gel aged, the irreversibility of the isotherms decreased significantly and, at $\tau > 10$ h, it completely disappeared. Therefore, it is believed that zirconia gel aging resulted in an increase in the effective sizes of micropores, so that O_2 molecules easily diffused into the porous space in this case. A capillary-condensation hysteresis, which is usually observed for

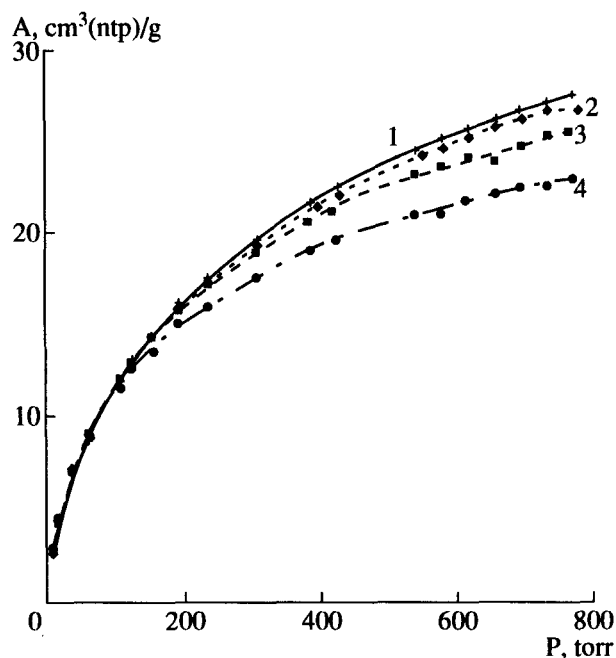


Fig. 1. Adsorption isotherms of H_2 at 77.4 K on ZrO_2 xerogels precipitated at 80°C and pH (1) 7, (2) 6, (3) 5, and (4) 4.

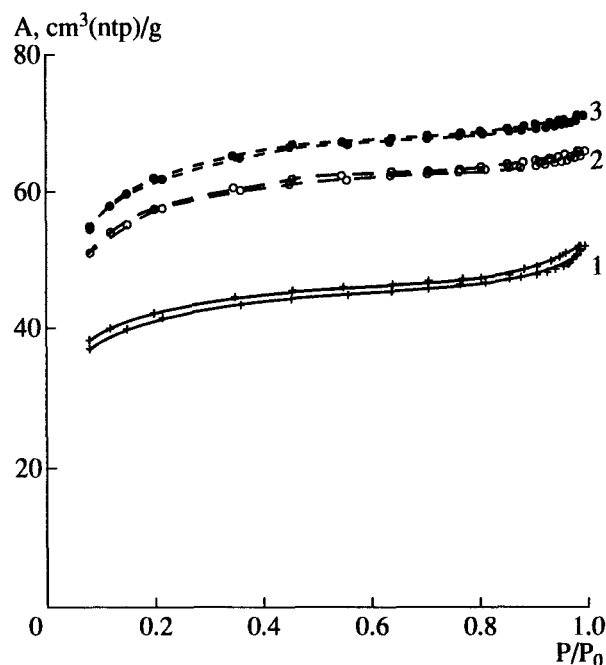


Fig. 2. Adsorption isotherms of O_2 at 77.4 K on zirconia xerogel samples (1) freshly precipitated at pH 4 and then aged for (2) 5 and (3) 10 h.

Table 2. Parameters of the microporous structure of ZrO_2 xerogels precipitated at pH 4 and then aged (calculated from the adsorption isotherms of oxygen)

τ , h	S_α , m ² /g	V_μ , cm ³ /g	$V_{\mu+s\mu}^*$, cm ³ /g	$S_\alpha(O_2)/S_\alpha(N_2)$	$V_{s\mu}^{**}$, cm ³ /g
0	64	0.030	0.048	1.19	0.018
3	100	0.034	0.067	1.18	0.033
5	103	0.035	0.070	1.20	0.035
10	117	0.037	0.076	1.27	0.039
22	115	0.035	0.072	1.24	0.037

* Total volume of micro- and supermicropores.

** Volume of supermicropores.

a noticeable volume of mesopores, was absent from the adsorption isotherms as well. The absence of reversible capillary condensation was proved by the linearity of comparative plots over a wide range of adsorbate pressures.

The parameters of the texture of ZrO_2 xerogels calculated from the adsorption isotherms of oxygen and nitrogen are summarized in Tables 2 and 3, respectively. It follows from these tables that S_α and the accessible volume of micropores V_μ increased with aging. The volumes V_μ determined from adsorption isotherms of O_2 and N_2 were in good agreement, whereas the surface area S_α measured by the adsorption of oxygen was larger than the corresponding value obtained from the

Table 3. Parameters of the texture of ZrO_2 xerogels precipitated at pH 4 and then aged (calculated from adsorption isotherms of N_2)

τ , h	S_α , m ² /g	V_μ , cm ³ /g	V_s^* , cm ³ /g	V_{me}^{**} , cm ³ /g	ϵ^{***}
0	54	0.029	0.071	0.033	0.22
3	86	0.034	0.086	0.035	0.25
5	87	0.037	0.089	0.033	0.26
10	92	0.040	0.094	0.033	0.27
22	93	0.036	0.099	0.044	0.28

* Limiting volume of the adsorption space.

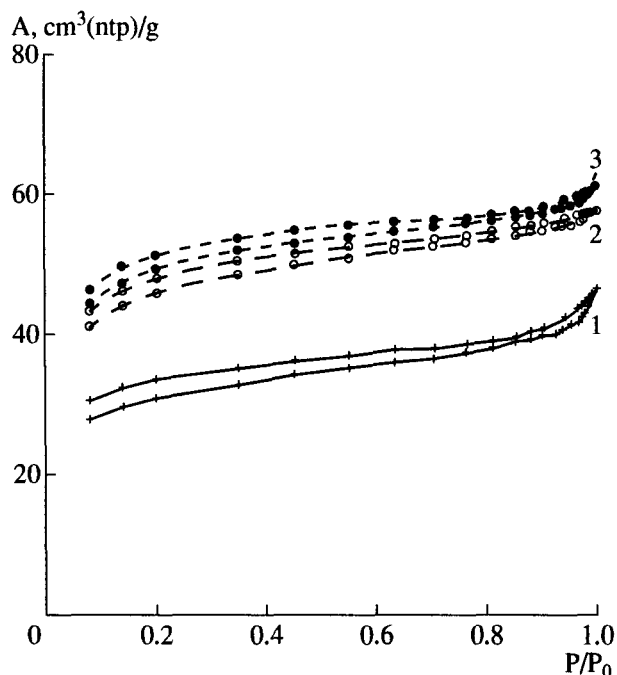
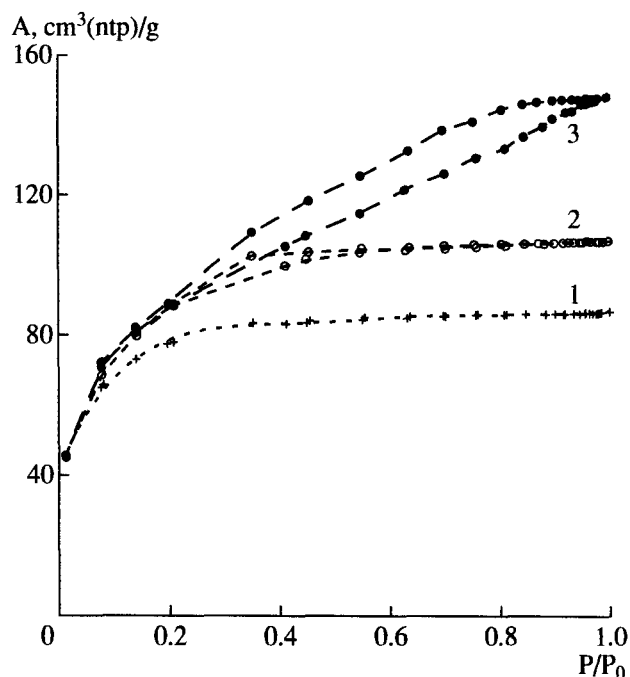
** Volume of mesopores.

*** Total porosity.

adsorption of N_2 . The ratios of these parameters are given in Table 2. Earlier, we revealed a similar phenomenon for the microporous structure of tin dioxide [9].

Table 4 presents similar data for the set of ZrO_2 samples precipitated at different pH in the range from 5 to 7 at 80°C. As follows from Fig. 4, the samples synthesized under these conditions differed in texture. With an increase in pH of precipitation (pH > 5), the volume of mesopores noticeably increased, as is evident from the typical capillary-condensation hysteresis in the adsorption isotherms of oxygen. The adsorption isotherms of nitrogen were similar.

Figure 5 presents the ratio between surface areas found from the adsorption isotherms of oxygen and

**Fig. 3.** Adsorption isotherms of N_2 at 77.4 K on zirconia xerogel samples (1) freshly precipitated at pH 4 and then aged for (2) 5 and (3) 10 h.**Fig. 4.** Adsorption isotherms of O_2 at 77.4 K on ZrO_2 xerogels precipitated at 80°C and pH 5 (1) 5, (2) 6, and (3) 7.

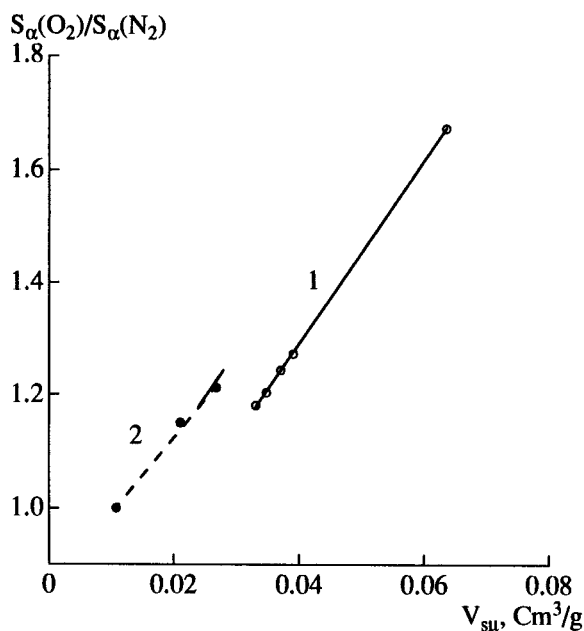


Fig. 5. Ratio between $S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2)$ and the volume of supermicropores measured from the oxygen adsorption in the samples of (1) zirconia and (2) tin dioxide [9].

nitrogen as a function of the supermicropore volume determined by the oxygen adsorption using the comparison method at $P/P_0 = 0.8-0.9$. The surface area of macropores S_m (this magnitude is quite small when the volume of mesopores is insignificant) on which layer-by-layer adsorption continued and the total volume of micro- and supermicropores $V_{\mu + s\mu}$ already occupied by adsorbate can be calculated by this procedure. The volume of supermicropores was calculated by the relation $V_{s\mu} = (V_{\mu + s\mu} - V_{\mu})$ (see Tables 2 and 4). With the samples that were synthesized at $\text{pH} > 5$ and possessed a significant volume of mesopores, this procedure failed (Table 4). The data obtained earlier for the SnO_2 sample [9] are also demonstrated in Fig. 5.

Figure 5 shows that a reliable linear correlation between the parameters under consideration exists (experimental data were processed by the least-squares method). The sample that was precipitated at $\text{pH} 4$ and not aged (the data for it are omitted from Fig. 5) is an exception. Recall that, for this sample, the adsorption isotherms of O_2 were considerably irreversible over the entire range of relative pressures; therefore, the microporous space might be filled incompletely.

The experimental dependence obtained is described by the simple linear equation

$$S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2) = 1 + k(V_{s\mu} - V_{s\mu}^*),$$

where k is the slope equal to 15.9. The calculated limiting value $V_{s\mu}^*$ defined as the volume of supermicropores at which $S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2) = 1$ was $\sim 0.022 \text{ cm}^3/\text{g}$. It should be noted that the data for ZrO_2 samples obtained under essentially different conditions are described by the common experimental relationship. Because the coefficient k equal to 15.9 was rather close to the value of 13.6 obtained from the examination of experimental data for tin dioxide [9], it may be stated that the relationship is quite universal and that k only slightly depends on the chemical nature of the oxide surface. At the same time, the limiting value of $V_{s\mu}^*$ for SnO_2 equaled $\sim 0.011 \text{ cm}^3/\text{g}$. Let us consider the possible reasons for the occurrence of such correlations.

The fact that surface areas increased with an increase in the volume of supermicropores is quite clear. However, up to the limiting value of $V_{s\mu}^*$, the surface areas measured by N_2 and O_2 adsorption equally increased, while at higher $V_{s\mu}$, the value of $S_{\alpha}(\text{O}_2)$ increased at a higher rate. The "advance" coefficient k remained unchanged for different oxide systems and was close to 15, whereas $V_{s\mu}^*$, which apparently reflected the geometric details of the microporous space was different for these systems.

A good agreement between the volumes of micropores V_{μ} measured by vapor adsorption of both adsorbates may be indicative of either unchanged densities of sorbed molecules under these conditions, which agrees with the so-called Gurvich rule [16], or almost the same change in them. At the same time, even if the arrangement of adsorbate molecules in larger supermicropores is accompanied by changes in their packing density, these changes are different.

It is known that the filling of true micropores proceeds by the mechanism of volume filling, while adsorption in the bulk of supermicropores appears to occur predominantly in layers [17-19]. It may be assumed that the fundamental dependence of the adsorption mechanism on the pore size of a sorbent leads to a different behavior of adsorbate molecules in the hindered microporous space.

Table 4. Parameters of the texture of ZrO_2 xerogels precipitated at $\text{pH} 5-7$ and then aged (calculated from the adsorption isotherms of N_2 and O_2)

Precipitation pH	$S_{\alpha}(\text{N}_2)$, m^2/g	$V_{\mu}(\text{N}_2)$, cm^3/g	$S_{\alpha}(\text{O}_2)$, m^2/g	$V_{\mu}(\text{O}_2)$, cm^3/g	$V_{s\mu}(\text{O}_2)$, cm^3/g	$S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2)$
5	111	0.037	186	0.034	0.064	1.67
6	221	0.013	300	0.011	—	1.35
7	294	0.011	310	0.010	—	1.05

In fact, the mobility of molecules in the adsorption layer determined by the lifetime of an adsorbed molecule is given by the adsorption energy [20]. A distinctive behavior of adsorbates in the pores of medium size should be due to a change from volume filling of micropores with a higher adsorption potential to layer-by-layer adsorption in mesopores. Molecules of different size exhibit dissimilar surface mobility in the adsorption layer. This manifested itself in a different change in adsorption by the unit surface of supermicropores (α) to the vapors of different adsorbents, including N_2 and O_2 .

Hence, it may be assumed that relative changes in α are reflected by k . In this case, the existence of the above linear dependence (Fig. 5) is sufficiently clear.

The conclusion can be made that the formation of the microporous ZrO_2 structure under the cited conditions of synthesis depends on the pH of precipitation. An increase in pH from 4 to 7 results in a decrease in the volume of micropores and in a simultaneous increase in the surface area of supermicropores and, at $pH > 5$, mesopores. Gel aging is accompanied by additional rearrangement that results in an increase in the micropore sizes and an insignificant growth of their overall volume. The limiting volume of xerogel adsorption space V_s and the total porosity ϵ also increase (Table 3).

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